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(54) **EXTRACTION SOLVENT CONTROL FOR REDUCING STABLE EMULSIONS**

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See application file for complete search history.

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(57) **ABSTRACT**

Disclosed herein are methods for recovering diphosphite-containing compounds from mixtures comprising organic mononitriles and organic dinitriles, using liquid-liquid extraction. Also disclosed are treatments to enhance extractability of the diphosphite-containing compounds.

21 Claims, 2 Drawing Sheets

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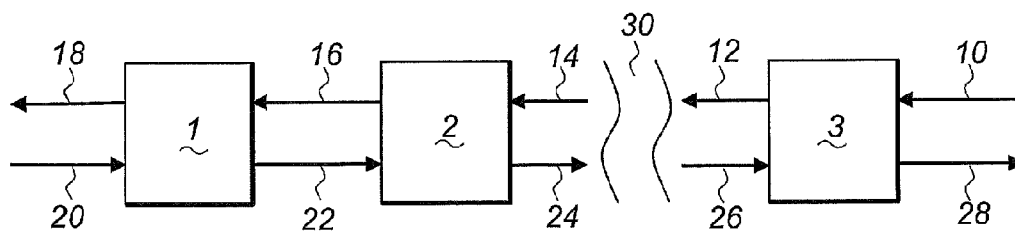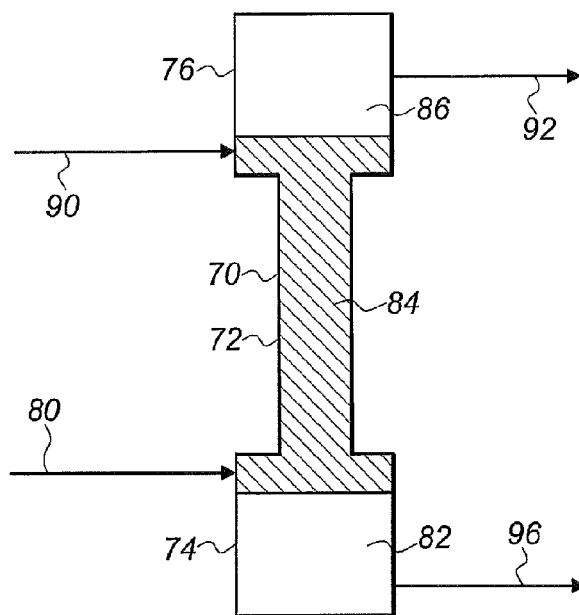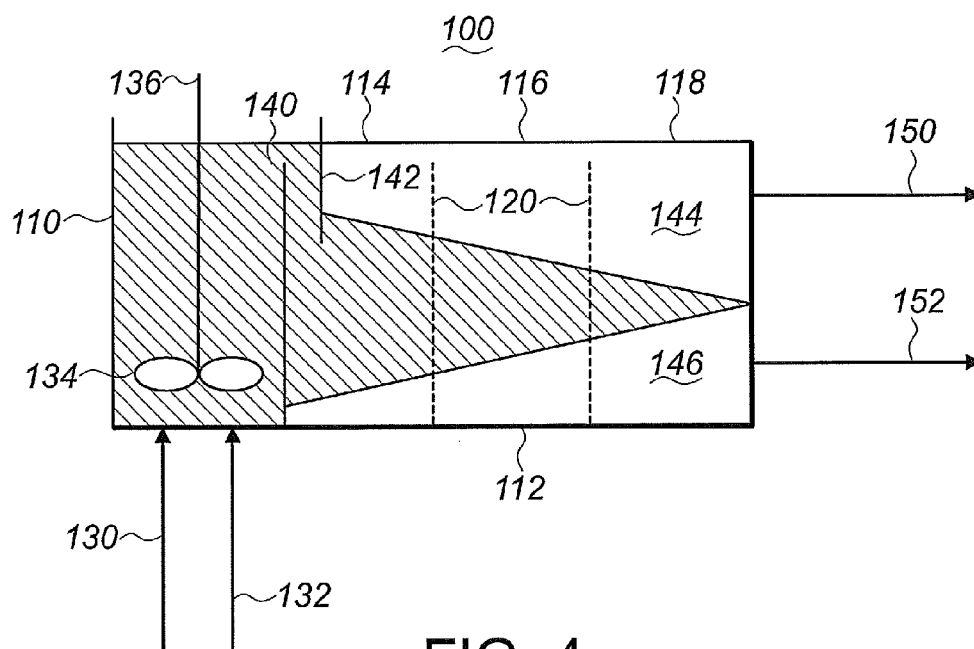
FIG. 1
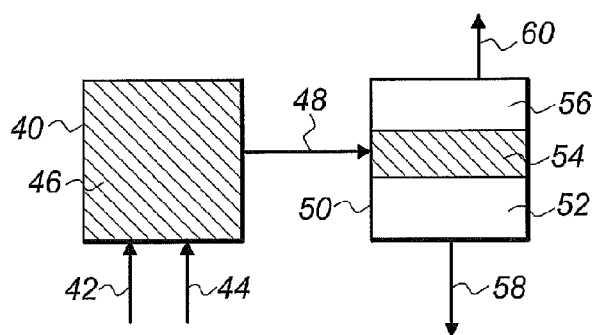
FIG. 2

FIG. 3

FIG. 4

EXTRACTION SOLVENT CONTROL FOR REDUCING STABLE EMULSIONS

RELATED APPLICATION

This application claims benefit to Provisional Application No. 61/578,535 filed on Dec. 21, 2011 which is herein incorporated by reference in its entirety.

FIELD OF THE INVENTION

The invention relates to recovery of catalyst and ligand from a hydrocyanation reaction product mixture comprising organic dinitriles using liquid-liquid extraction.

BACKGROUND OF THE INVENTION

It is well known in the art that complexes of nickel with phosphorous-containing ligands are useful as catalysts in hydrocyanation reactions. Such nickel complexes using monodentate phosphites are known to catalyze hydrocyanation of butadiene to produce a mixture of pentenenitriles. These catalysts are also useful in the subsequent hydrocyanation of pentenenitriles to produce adiponitrile, an important intermediate in the production of nylon. It is further known that bidentate phosphite and phosphinite ligands can be used to form nickel-based catalysts to perform such hydrocyanation reactions.

U.S. Pat. No. 3,773,809 describes a process for the recovery of Ni complexes of organic phosphites from a product fluid containing organic nitriles produced by hydrocyanating an ethylenically unsaturated organic mononitrile such as 3-pentenenitrile through extraction of the product fluid with a paraffin or cycloparaffin hydrocarbon solvent. Similarly, U.S. Pat. No. 6,936,171 to Jackson and McKinney discloses a process for recovering diphosphite-containing compounds from streams containing dinitriles.

U.S. Pat. No. 4,339,395 describes the formation of an interfacial rag layer during extended periods of continuous extraction of certain phosphite ligands. The '395 patent notes that the interfacial rag hinders, if not halts, the phase separation. Because the process is operated continuously, the rag must be removed continuously from the interface as it accumulates to avoid interrupting operation. To solve this problem for the disclosed components, the '395 patent discloses the addition of minor amounts of substantially water-free ammonia.

SUMMARY OF THE INVENTION

This process recovers diphosphite-containing compounds from a mixture comprising diphosphite-containing compounds, organic mononitriles and organic dinitriles.

Disclosed is a process for recovering diphosphite-containing compounds from a feed mixture comprising diphosphite-containing compounds, organic mononitriles, organic dinitriles and a Lewis acid in a multistage countercurrent liquid-liquid extractor with extraction solvent comprising aliphatic hydrocarbon, cycloaliphatic hydrocarbon or a mixture of aliphatic and cycloaliphatic hydrocarbon. The process comprises:

a) flowing the feed mixture to the first stage of the multistage countercurrent liquid-liquid extractor; and

b) contacting the feed mixture with extraction solvent in the multistage countercurrent liquid-liquid extractor;

wherein the first stage of the multistage countercurrent liquid-liquid extractor comprises a mixing section and a set-

tling section, wherein a light phase separates from a heavy phase in the settling section, wherein a Lewis base is added to the mixing section of the first stage of the multistage countercurrent liquid-liquid extractor, wherein the light phase comprises extraction solvent and extracted diphosphite-containing compounds, wherein the heavy phase comprises organic mononitriles, organic dinitriles and a complex of said Lewis acid and said Lewis base, wherein at least a portion of the light phase is withdrawn from the settling section and treated to recover diphosphite-containing compounds extracted into the light phase, wherein at least a portion of the heavy phase is passed to the second stage of the multistage countercurrent liquid-liquid extractor.

The mixing sections of the stages of the multistage countercurrent liquid-liquid extractor form an intimate mixture of unseparated light and heavy phase. This intimate mixture comprises an emulsion phase. The emulsion phase may or may not comprise particulate solid material. This emulsion phase separates into a light phase and a heavy phase in the settling sections of the stages, including the first stage. Accordingly, the settling sections of the stages will contain at least some emulsion phase located between the upper light phase and the lower heavy phase. This emulsion phase tends to reduce in size over time. However, in some instances settling takes longer than desired or the emulsion phase never fully separates into a light phase and a heavy phase. This separation problem may be particularly troublesome in the first stage of a multistage countercurrent liquid-liquid extractor.

Addition of Lewis base to the mixing section of the first stage has been found to result in enhanced settling of the emulsion phase. For example, this addition may result in the reduction of the size of the emulsion phase in the settling section, wherein the size of the emulsion phase is based upon the size of the emulsion phase in the absence of addition of Lewis base. Enhanced settling in the settling section may also be measured as an increased rate of settling, based upon the rate of settling in the absence of addition of Lewis base.

Another problem, which may be solved by addition of Lewis base is formation of rag and build-up of a rag layer the settling section. Rag formation is discussed in U.S. Pat. No. 4,339,395 and U.S. Pat. No. 7,935,229. Rag comprises particulate solid material, and may be considered to be a form of an emulsion phase, which is particularly stable in the sense that it does not dissipate in a practical amount of time for conducting an extraction process. Rag may form in the mixing section or the settling section of an extraction stage, particularly the first stage of a multistage countercurrent liquid-liquid extractor. In the settling section, the rag forms a layer between the heavy phase and the light phase. The formation of a rag layer in the settling section inhibits proper settling of the heavy phase and the light phase. The formation of a rag layer may also inhibit the extraction of diphosphite-containing compounds from the heavy phase into the light phase. In a worst case scenario, rag can build up to extent of completely filling a separation section, necessitating shut down of the extraction process to clean out the settling section. It has been found that addition of Lewis base to the mixing section may reduce or eliminate the size of a rag layer or reduce its rate of formation, based upon the size and rate of formation of the rag layer in the absence of addition of Lewis base.

Accordingly, addition of Lewis base to the mixing section of the first stage of a multistage countercurrent extractor may achieve at least one of the following results: (a) a reduction in the size of an emulsion phase in the settling section, based upon the size of the emulsion phase in the absence of addition
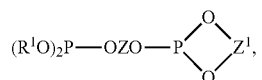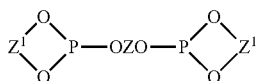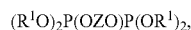
of Lewis base; (b) an increase in the rate of settling in the settling section, based upon the rate of settling in the absence of addition of Lewis base; (c) an increase in the amount of diphosphite-containing compounds in the light phase, based upon the upon the amount of diphosphite-containing compounds in the light phase in the absence of addition of Lewis base; (d) a partial or total reduction in the size of a rag layer in the settling section, based upon the size of a rag layer in the settling section in the absence of addition of Lewis base; and (e) reduction in the rate of formation of a rag layer in the settling section, based upon the rate of formation of a rag layer in the settling section in the absence of addition of Lewis base.

In one embodiment, Lewis base is cofed to the mixing section along with the feed mixture comprising diphosphite-containing compounds, organic mononitriles, organic dinitriles and Lewis acid. In another embodiment, Lewis base is separately fed to the mixing section apart from the feed mixture comprising diphosphite-containing compounds, organic mononitriles, organic dinitriles and Lewis acid and the extraction solvent feed.

A particular example of a Lewis acid, which may be present in the feed to the extractor, is $ZnCl_2$.
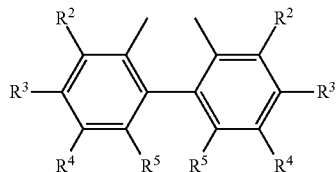
The extraction solvent feed from the second stage may comprise at least 1000 ppm, for example, from 2000 to 5000 ppm, of diphosphite-containing compounds. The extraction solvent feed from the second stage may comprise at least 10 ppm, for example, from 20 to 200 ppm, of nickel.

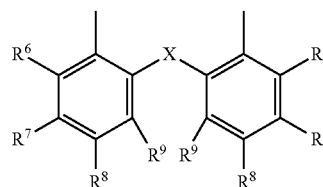The diphosphite-containing compound may be a diphosphite ligand selected from the group consisting of:

$$(R^1O)_2P(OZO)P(OR^1)_2, \quad \text{I}$$

II

$$(R^1O)_2P\text{—}OZO\text{—}P \quad \text{III}$$

and

wherein in I, II and III, R^1 is phenyl, unsubstituted or substituted with one or more C_1 to C_{12} alkyl or C_1 to C_{12} alkoxy groups; or naphthyl, unsubstituted or substituted with one or more C_1 to C_{12} alkyl or C_1 to C_{12} alkoxy groups; and wherein Z and Z^1 are independently selected from the group consisting of structural formulae IV, V, VI, VII, and VIII:
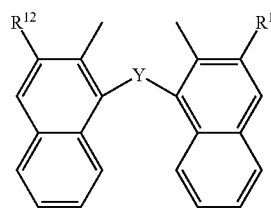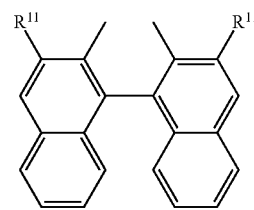
IV

-continued

V

and wherein

R^2, R^3, R^4, R^5, R^6, R^7, R^8, and R^9 are independently selected from the group consisting of H, C_1 to C_{12} alkyl, and C_1 to C_{12} alkoxy;

X is O, S, or $CH(R^{10})$;

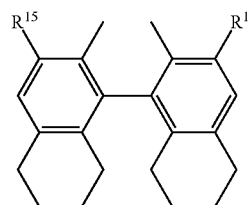R^{10} is H or C_1 to C_{12} alkyl;

VI

VII

and wherein

R^{11} and R^{12} are independently selected from the group consisting of H, C_1 to C_{12} alkyl, and C_1 to C_{12} alkoxy and CO_2R^{13},

R^{13} is C_1 to C_{12} alkyl, or C_6 to C_{10} aryl unsubstituted or substituted with C_1 to C_4 alkyl;

Y is O, S, or $CH(R^{14})$;

R^{14} is H or C_1 to C_{12} alkyl;

VIII

wherein

R^{15} is selected from the group consisting of H, C_1 to C_{12} alkyl, and C_1 to C_{12} alkoxy and CO_2R^{16},

R^{16} is C_1 to C_{12} alkyl, or C_6 to C_{10} aryl, unsubstituted or substituted with C_1 to C_4 alkyl,

and wherein

for structural formulae I through VIII, the C_1 to C_{12} alkyl, and C_1 to C_{12} alkoxy groups may be straight chain or branched.

At least a portion of the diphosphite ligand may be complexed with zero valent Ni.

At least one stage of the extraction may be carried out above 40° C.

The Lewis base may be a monodentate triarylphosphite, wherein the aryl groups are unsubstituted or substituted with alkyl groups having 1 to 12 carbon atoms, and wherein the aryl groups may be interconnected.

The Lewis base may optionally be selected from the group consisting of:

a) anhydrous ammonia, pyridine, alkylamine, dialkylamine, trialkylamine wherein the alkyl groups have 1 to 12 carbon atoms; and

b) polyamine.

If the Lewis base is a polyamine, the polyamine may comprise at least one selected from hexamethylene diamine, and dimers and trimers of hexamethylene diamine, for example, bis-hexamethylene triamine.

The Lewis base may optionally comprise a basic ion exchange resin, for example, Amberlyst 21® resin.

One example of a suitable cyclic alkane extraction solvent is cyclohexane.

At least a portion of the process may be carried out in an extraction column or a mixer-settler.

The feed mixture may be an effluent stream from a hydrocyanation process, for example, a process for hydrocyanating 3-pentenenitrile, a process for the single hydrocyanation of 1,3-butadiene to pentenenitriles or a process for the double hydrocyanation of 1,3-butadiene to adiponitrile.

The first stage of the multistage countercurrent liquid-liquid extractor may take place in an extraction column. The entire column may be considered to be a settling section comprising a mixing section between a heavy phase collection section and a light phase collection section. Heavy phase may be recycled to the mixing section of the extraction column.

The first stage of the multistage countercurrent liquid-liquid extractor may take place in an mixer-settler. The mixer-settler may comprise a settling section which is separate from the mixing section. Recycled heavy stream may be recycled upstream from the point of withdraw of the recycled heavy stream.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a diagram showing the flow of fluids through a multistage countercurrent liquid-liquid extractor.

FIG. 2 is a diagram showing a mixing section and a settling section of a stage of a multistage countercurrent liquid-liquid extractor.

FIG. 3 is a diagram showing an extraction column.

FIG. 4 is a diagram showing a mixing/settling apparatus having three chambers in the settling section.

DETAILED DESCRIPTION OF THE INVENTION

The processes of the present invention involve methods for recovering diphosphite-containing compounds from a mixture comprising diphosphite-containing compounds and organic dinitriles, using liquid-liquid extraction.

FIG. 1 is a diagram of a multistage countercurrent liquid-liquid extractor. Lines in FIG. 1 represent flow of materials, rather than any particular type of equipment, such as pipes. Similarly, squares in this diagram represent stages or sections for mixing and settling, rather than any particular type of equipment.

Three stages are depicted in FIG. 1. The first stage is depicted by mixing and settling section 1. The second stage is depicted by mixing and settling section 2. The final stage is

depicted by mixing and settling section 3. Gap 30 represents a space where additional stages may be inserted. For example, one or more, for example, from one to four, mixing and settling sections may be inserted in gap 30 between mixing and settling section 2 and mixing and settling section 3.

In FIG. 1, a fresh extraction solvent feed, for example, cyclohexane, is introduced into the multistage countercurrent extractor via line 10. The extraction solvent or light phase exiting from mixing settling section 3 passes through line 12 to the next stage of the multistage extractor. In a multistage countercurrent liquid-liquid extractor having three stages, extraction solvent in line 12 would pass directly into stage 2 via line 14. Extraction solvent from stage 2 passes through line 16 to stage 1. The extraction solvent comprising extracted diphosphite-containing compounds passes out of the stage 1 mixing and settling section through line 18.

A feed comprising diphosphite-containing compounds is fed into the stage 1 mixer and settler via line 20. The feed further comprises a mixture comprising organic mononitriles and dinitriles, which is immiscible with the extraction solvent. The feed further comprises a Lewis acid. In stage 1, a portion of the diphosphite-containing compounds is extracted into the extraction solvent which exits stage 1 via line 18. The immiscible dinitrile and mononitrile mixture or the heavy phase is removed from the stage 1 mixing and settling section by line 22 and is passed into the stage 2 mixing and settling section. A portion of the diphosphite-containing compounds is extracted into the light phase in the stage 2 mixing and settling section. The heavy phase exits the stage 2 mixing and settling section by line 24. Similarly, if there are additional stages in gap 30 shown in FIG. 1, extraction of diphosphite-containing compounds will take place in such intermediate stages in a similar manner to that taking place in stage 2.

After the heavy phase passes through the first stage and any intermediate stages, it passes through the final stage mixing and settling section 3. In particular, the heavy phase is introduced into mixing and setting section 3 through line 26. After passing through the final stage mixing and settling section 3, the heavy phase exits via line 28.

A two-stage multistage countercurrent liquid-liquid extractor is represented in FIG. 1 by mixing and settling sections 1 and 2; lines 14, 16 and 18 showing the direction of extraction solvent flow; and lines 20, 22 and 24 showing the direction of heavy phase flow. In a two-stage multistage counter current liquid-liquid extractor, mixing and settling section 3; lines 10, 12, 26 and 28; and gap 30 are omitted. In the two stage countercurrent liquid-liquid extractor, extraction solvent comprising extracted diphosphite-containing compounds passes from the extractor through line 18, and extracted heavy phase, i.e. raffinate, passes from the extractor through line 24.

Thus, it can be seen that the multistage countercurrent liquid-liquid extractor comprises two or more stages with countercurrent flow of extraction solvent and heavy phase. In view of the direction of flow of light and heavy phase through the stages of extraction, it will be appreciated that the concentration of solute, e.g., diphosphite-containing compound, is highest in both the light and heavy phases of the first stage and lowest in the light and heavy phases of the final stage.

FIG. 2 is a diagrammatic representation of one type of a mixing and settling section, also referred to herein as a mixer-settler. This type of mixer-settler may be used in any of the stages shown in FIG. 1. This mixer-settler comprises a mixing section 40 and a settling section 50. The mixing section 40 and the settling section 50 are separate. All of the effluent from the mixing section 40 flows into the settling section 50. Fluid from the mixing section 40 flows through the settling

section **50** in a in a horizontal manner, although there is also no restriction of movement of fluids vertically throughout the settling section **50**.

An extraction solvent is introduced into the mixing section **40** by line **42**. A feed comprising diphosphite-containing compounds is introduced into the mixing section **40** by line **44**. Alternatively, the contents of lines **42** and **44** may be combined upstream of the mixing section **40** and introduced into mixing section **40** through a single inlet. These two feeds are mixed in the mixing section **40** to provide a mixed phase comprising an emulsion phase represented in FIG. **2** by shaded area **46**.

Line **48** represents the flow of mixed phase **46** from the mixing section **40** into the settling section **50**. As depicted in FIG. **2**, there are three phases in the settling section **50**, including a heavy phase **52**, a mixed phase **54**, and a light phase **56**. The heavy phase **52** is depleted in diphosphite-containing compounds, insofar as it has a lower concentration of diphosphite-containing compounds as compared with the concentration of diphosphite-containing compounds in feed **44**, due to the extraction of diphosphite-containing compounds into the light phase **56**. Correspondingly, the light phase **56** is enriched in diphosphite-containing compounds, insofar as it has a higher concentration of diphosphite-containing compounds as compared with the concentration of diphosphite-containing compounds in extraction solvent feed **42**, due to the extraction of diphosphite-containing compounds into the light phase **56**. At least a portion of the heavy phase **52** exits the settling section **50** via line **60**. At least a portion of the light phase **56** is removed from the settling section **50** via line **58**.

Although not shown in FIG. **2**, which is diagrammatically shows the flow of fluids, it will be understood that each of the mixing section **40** and the settling section **50** may comprise one or more stages, subsections, compartments or chambers. For example, settling section **50** may include more than one chamber between the point of introduction of the mixed phase **46** through line **48** and the point of withdrawal of light phase and heavy phase through lines **58** and **60**. Horizontal extension between the point of introduction of the mixed phase **46** through line **48** and the point of withdrawal of light and heavy phases through lines **58** and **60** promotes settling of the light and heavy phases **56** and **52**. The size of the mixed phase **54** may become progressively smaller as fluids settle and flow through the chamber. For example, the final chamber from where fluids are removed may include little or no mixed phase **54**. It will further be understood that mixing section **40** may include one or more types of mixing apparatus, such as an impeller, not shown in FIG. **2**.

FIG. **3** provides a representation of another type of apparatus for use as a mixing and settling section. The type of apparatus **70** shown in FIG. **3** is referred to herein as an extraction column. This extraction column **70** includes a mixing section **72**, a heavy phase collection section **74** and a light phase collection section **76**. The entire column **70** may be considered to be a settling section with a mixing section between collection section **74** and collection section **76**. In extraction column **70** the mixing section **72** is part of the settling section. An extraction solvent is introduced into column **70** through line **80**. A heavier phase comprising a diphosphite-containing compound is introduced into column **70** through line **90**. As the light phase passes upward through the column, and the heavy phase passes downward through the column, a mixture of the two phases is formed in mixing section **72**. This mixture is represented in FIG. **3** as shaded mixed phase **84**. This mixed phase **84** may comprise an emulsion phase. The point of introduction of heavy phase through

line **90** should be sufficiently above the point of introduction of the light phase to allow for sufficient mixing of the two phases in the mixing section resulting in the extraction of diphosphite-containing compounds into the light phase. The intimate mixing of light and heavy phase in mixing section **72** may be promoted by mechanical or static mixing apparatus not shown in FIG. **3**. For example, mixing section **72** may comprise baffles or perforated plates, not shown in FIG. **3**.

The heavy phase **82** settles into collection section **74** and passes out of the column **70** through line **96**. Light phase **86** settles in collection section **76** and passes from the column through line **92**.

FIG. **4** provides a representation of a mixer-settler **100** having a multistage settling section. Mixer-settler **100** has a mixing section **110** and a settling section **112**. In mixer-settler **100**, the mixing section **110** is separate from the settling section **112**. The settling section has three compartments, represented in FIG. **4** as sections **114**, **116**, and **118**. These sections are separated by coalescence plates **120**. The coalescence plates **120** may be designed to provide flow of separated light and heavy phases between chambers, while restricting the flow of emulsion phase between chambers. A feed comprising a diphosphite-containing compound is passed into the mixing section **110** via line **130**. The extraction solvent is introduced into mixing section **110** via line **132**. The mixing section **110** includes an impeller **134** mounted on shaft **136** to provide for mechanical mixing of fluids. Mixing of the feeds provides a mixed phase comprising an emulsion phase represented in FIG. **4** by shading **140**.

The mixed phase **140** flows into the settling section **112** as an overflow from the mixing section **110**. This mixed phase **140** is prevented from flowing directly into the light phase **144** by baffle plate **142**. As settling occurs in settling section **112**, the volume of the mixed phase **140** decreases, the volume of the light phase **144** increases, and the volume of the heavy phase **146** increases. Heavy phase **146** is removed from settling section **112**, in particular from chamber **118**, via line **152** and light phase **144** is removed from settling section **112**, in particular, from chamber **118**, via line **150**.

It is desirable for both a mononitrile and a dinitrile to be present in the countercurrent contactor. For a discussion of the role of monodentate and bidentate ligand in extraction of hydrocyanation reactor effluent streams, see U.S. Pat. No. 3,773,809 to Walter and U.S. Pat. No. 6,936,171 to Jackson and McKinney.

For the process disclosed herein, suitable molar ratios of mononitrile to dinitrile components include 0.01 to 2.5, for example, 0.01 to 1.5, for example 0.65 to 1.5.

Maximum temperature is limited by the volatility of the hydrocarbon solvent utilized, but recovery generally improves as the temperature is increased. Examples of suitable operating ranges are 40° C. to 100° C. and 50° C. to 80° C.

The controlled addition of monophosphite ligands may enhance settling. Examples of monophosphite ligands that may be useful as additives include those disclosed in Drinkard et al U.S. Pat. No. 3,496,215, U.S. Pat. No. 3,496,217, U.S. Pat. No. 3,496,218, U.S. Pat. No. 5,543,536, and published PCT Application WO 01/36429 (BASF).

As described herein, the addition of Lewis base compounds to a mixture comprising diphosphite-containing compounds, organic mononitriles and organic dinitriles enhances settling, especially when the mixture comprises a Lewis acid, such as $ZnCl_2$. Examples of suitable weak Lewis base compounds include water and alcohols. Suitable stronger Lewis base compounds include hexamethylene diamine, dimers and trimers of hexamethylene diamine, ammonia, aryl- or alkyl

amines, such as pyridine or triethylamine, or basic resins such as Amberlyst 21®, a commercially available basic resin made by Rohm and Haas. The addition of Lewis base may reduce or eliminate any inhibiting effect of Lewis acid on catalyst recovery.

The reaction product of Lewis acid with Lewis base may become entrained in the raffinate phase as it moves through the multistage countercurrent liquid-liquid extractor. In particular, this product may form a precipitate in the raffinate phase in the form of a complex of Lewis acid with Lewis base. However, this precipitate may exist as a dispersion of fine particles distributed throughout the raffinate phase. This precipitate may be removed by conventional techniques, such as filtration, centrifugation or distillation accompanied by removal of bottoms containing the precipitate, after the raffinate is removed from the last stage of the multistage countercurrent liquid-liquid extractor.

The diphosphite-containing compounds extracted by the processes described herein comprise bidentate phosphorus-containing ligands. These extracted ligands comprise free ligands (e.g., those which are not complexed to a metal, such as nickel) and those which are complexed to a metal, such as nickel. Accordingly, it will be understood that extraction processes described herein are useful for recovering diphosphite-containing compounds which are metal/ligand complexes, such as a complex of zero valent nickel with at least one ligand comprising a bidentate-phosphorus containing ligand.

Suitable ligands for extraction are bidentate phosphorous-containing ligands selected from the group consisting of bidentate phosphites, and bidentate phosphinites. Preferred ligands are bidentate phosphite ligands.

Diphosphite Ligands

Examples of bidentate phosphite ligands useful in the invention include those having the following structural formulae:
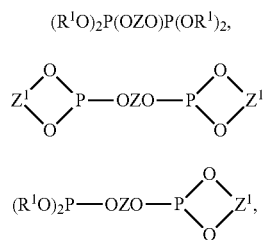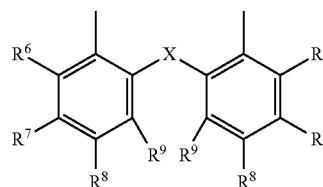
$$(R^1O)_2P(OZO)P(OR^1)_2, \qquad \text{I}$$

II

III

and
wherein in I, II and III, R^1 is phenyl, unsubstituted or substituted with one or more C_1 to C_{12} alkyl or C_1 to C_{12} alkoxy groups; or naphthyl, unsubstituted or substituted with one or more C_1 to C_{12} alkyl or C_1 to C_{12} alkoxy groups; and Z and Z^1 are independently selected from the group consisting of structural formulae IV, V, VI, VII, and VIII:

IV

-continued
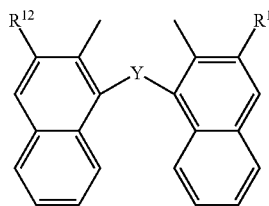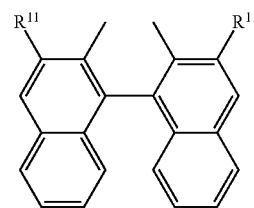

V

and wherein
R^2, R^3, R^4, R^5, R^6, R^7, R^8, and R^9 are independently selected from the group consisting of H, C_1 to C_{12} alkyl, and C_1 to C_{12} alkoxy;
X is O, S, or CH(R^{10});
R^{10} is H or C_1 to C_{12} alkyl;

VI

VII

and wherein
R^{11} and R^{12} are independently selected from the group consisting of H, C_1 to C_{12} alkyl, and C_1 to C_{12} alkoxy; and CO_2R^{13},
R^{13} is C_1 to C_{12} alkyl or C_6 to C_{10} aryl, unsubstituted or substituted. with C_1 to C_4 alkyl;
Y is O, S, or CH(R^{14});
R^{14} is H or C_1 to C_{12} alkyl;

VIII

wherein
R^{15} is selected from the group consisting of H, C_1 to C_{12} alkyl, and C_1 to C_{12} alkoxy and CO_2R^{16};
R^{16} is C_1 to C_{12} alkyl or C_6 to C_{10} aryl, unsubstituted or substituted with C_1 to C_4 alkyl.

In the structural formulae I through VIII, the C_1 to C_{12} alkyl, and C_1 to C_{12} alkoxy groups may be straight chain or branched.

Another example of a formula of a bidentate phosphite ligand that is useful in the present process is that having the Formula X, shown below
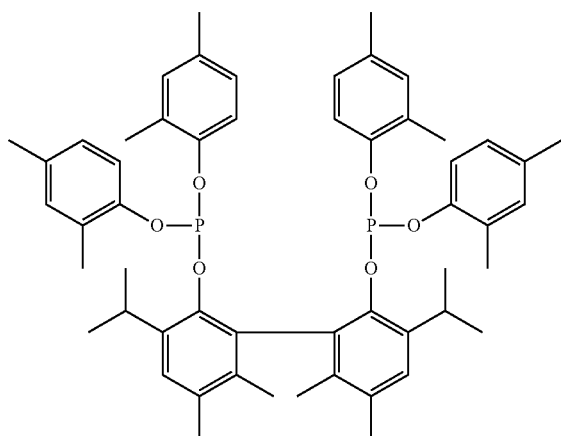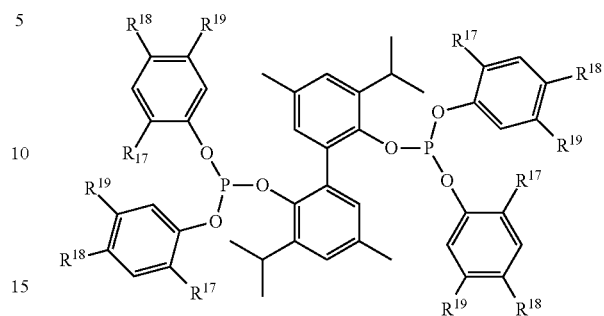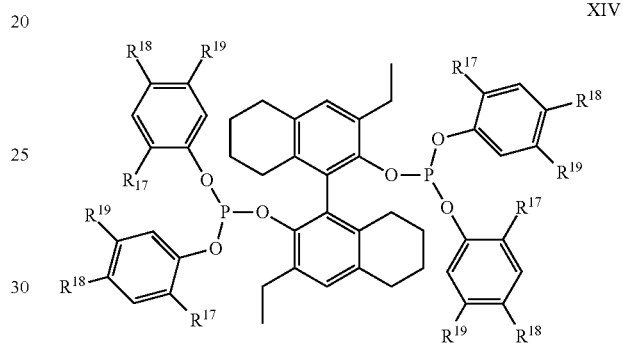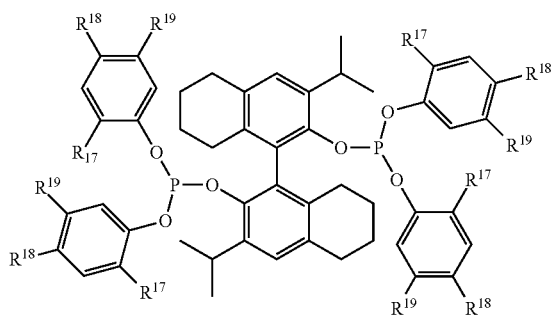
X

Further examples of bidentate phosphite ligands that are useful in the present process include those having the Formulae XI to XIV, shown below wherein for each formula, R^{17} is selected from the group consisting of methyl, ethyl or isopropyl, and R^{18} and R^{19} are independently selected from H or methyl:
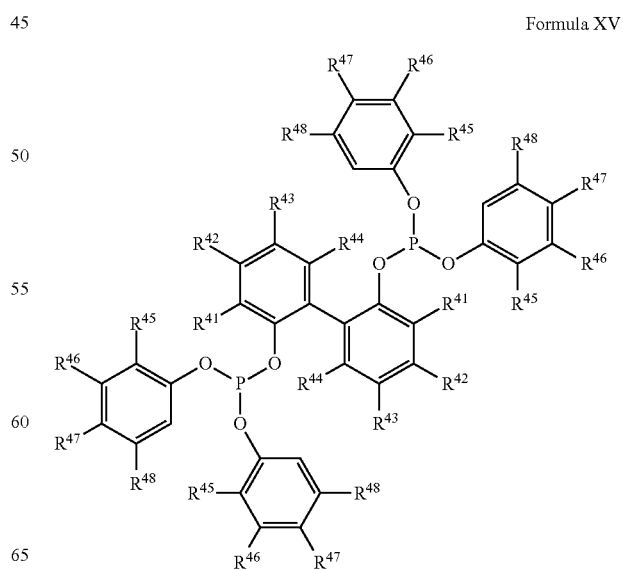
XI

XII

XIII

XIV

Additional examples of bidentate phosphite ligands that are useful in the present process include a ligand selected from a member of the group represented by Formulae XV and XVI, in which all like reference characters have the same meaning, except as further explicitly limited:
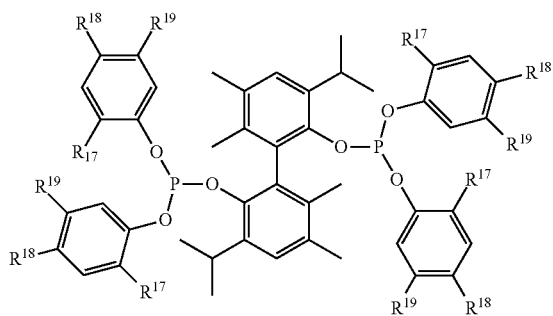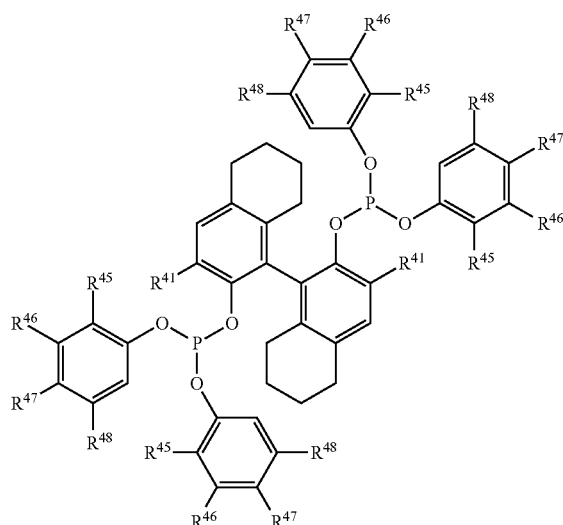
Formula XV

-continued

Formula XVI

wherein

R^{41} and R^{45} are independently selected from the group consisting of C_1 to C_5 hydrocarbyl, and each of R^{42}, R^{43}, R^{44}, R^{46}, R^{47} and R^{48} is independently selected from the group consisting of H and C_1 to C_4 hydrocarbyl.

For example, the bidentate phosphite ligand can be selected from a member of the group represented by Formula XV and Formula XVI, wherein

R^{41} is methyl, ethyl, isopropyl or cyclopentyl;
R^{42} is H or methyl;
R^{43} is H or a C_1 to C_4 hydrocarbyl;
R^{44} is H or methyl;
R^{45} is methyl, ethyl or isopropyl; and
R^{46}, R^{47} and R^{48} are independently selected from the group consisting of H and C_1 to C_4 hydrocarbyl.

As additional examples, the bidentate phosphite ligand can be selected from a member of the group represented by Formula XV, wherein

R^{41}, R^{44}, and R^{45} are methyl;
R^{42}, R^{46}, R^{47} and R^{48} are H; and
R^{43} is a C_1 to C_4 hydrocarbyl;
or
R^{41} is isopropyl;
R^{42} is H;
R^{43} is a C_1 to C_4 hydrocarbyl;
R^{44} is H or methyl;
R^{45} is methyl or ethyl;
R^{46} and R^{48} are H or methyl; and
R^{47} is H, methyl or tertiary-butyl;
or the bidentate phosphite ligand can be selected from a member of the group represented by Formula XVI, wherein

R^{41} is isopropyl or cyclopentyl;
R^{45} is methyl or isopropyl; and
R^{46}, R^{47}, and R^{48} are H.

As yet another example, the bidentate phosphite ligand may be represented by Formula XV, wherein R^{41} is isopropyl; R^{42}, R^{46}, and R^{48} are H; and R^{43}, R^{44}, R^{45}, and R^{47} are methyl.

It will be recognized that Formulae X to XVI are two-dimensional representations of three-dimensional molecules and that rotation about chemical bonds can occur in the mol-

ecules to give configurations differing from those shown. For example, rotation about the carbon-carbon bond between the 2- and 2'-positions of the biphenyl, octahydrobinaphthyl, and or binaphthyl bridging groups of Formulae X to XVI, respectively, can bring the two phosphorus atoms of each Formula in closer proximity to one another and can allow the phosphite ligand to bind to nickel in a bidentate fashion. The term "bidentate" is well known in the art and means both phosphorus atoms of the ligand are bonded to a single nickel atom.

Further examples of bidentate phosphite ligands that are useful in the present process include those having the formulae XX to LIII, shown below wherein for each formula, R^{17} is selected from the group consisting of methyl, ethyl or isopropyl, and R^{18} and R^{19} are independently selected from H or methyl:

XX
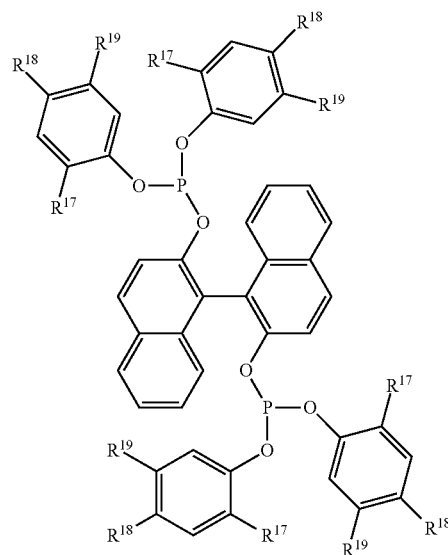
XXI
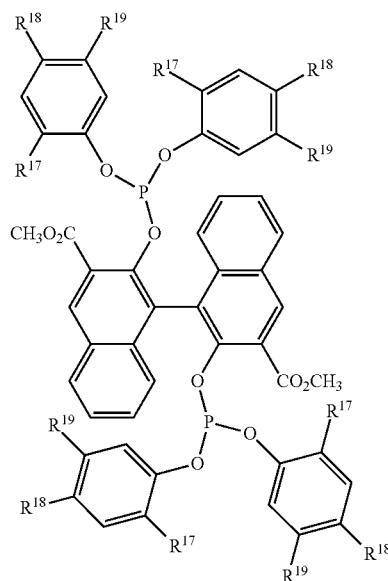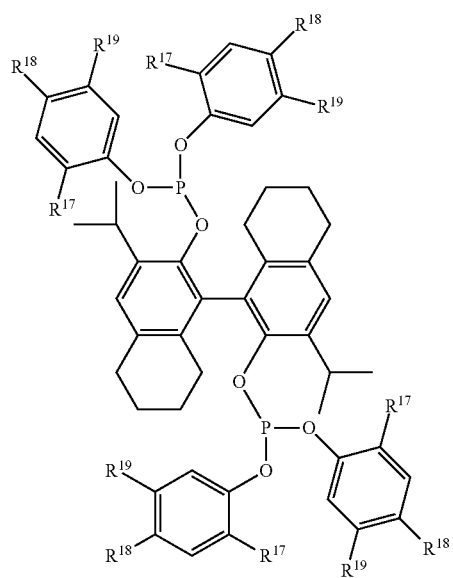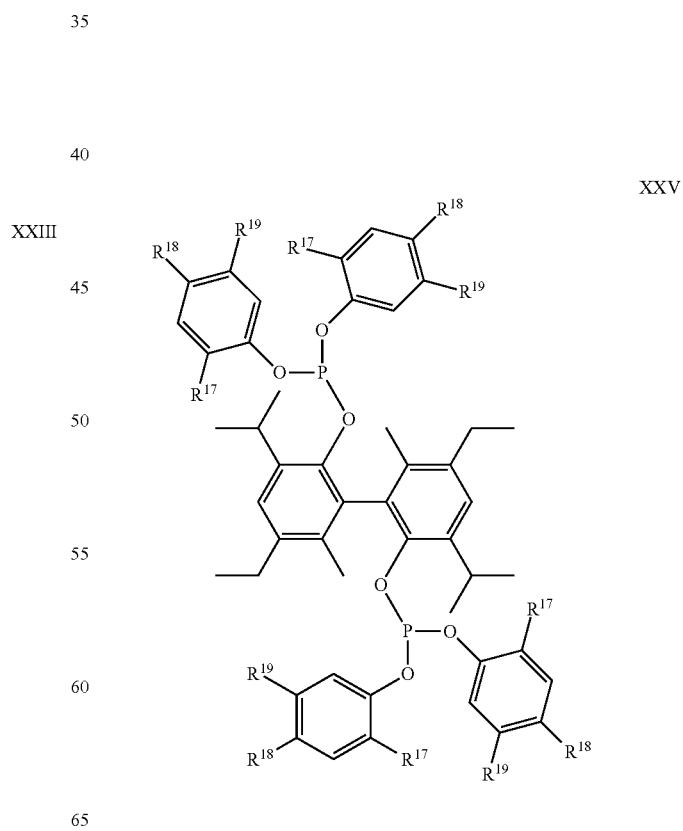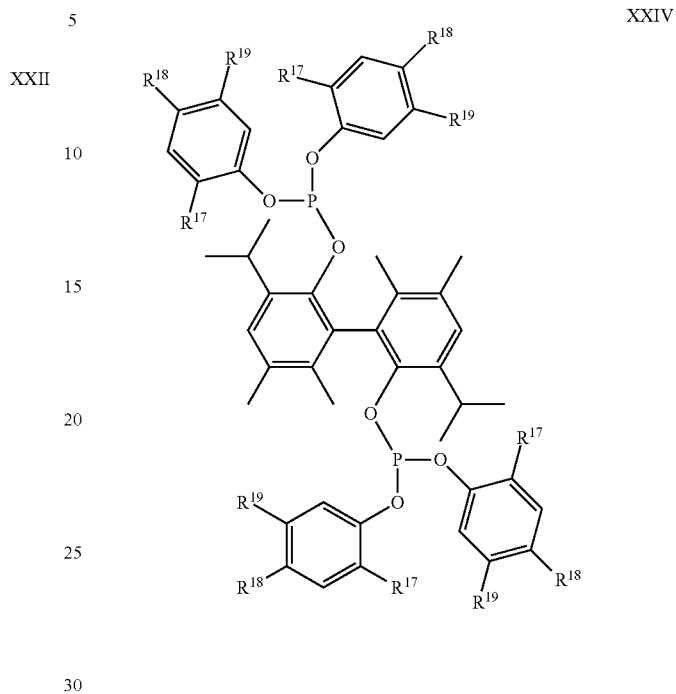
15
-continued

16
-continued

XXII

XXIV

XXIII

XXV

17
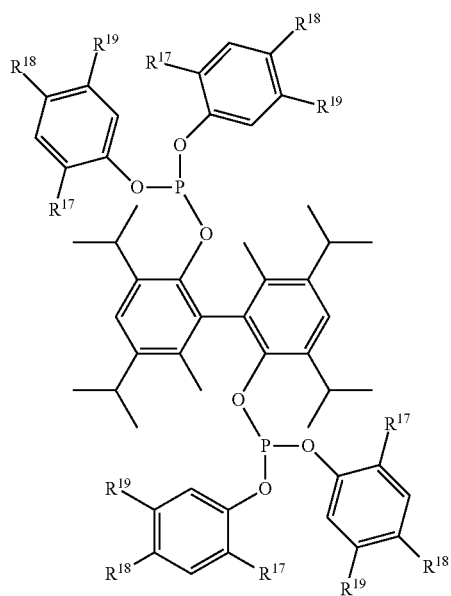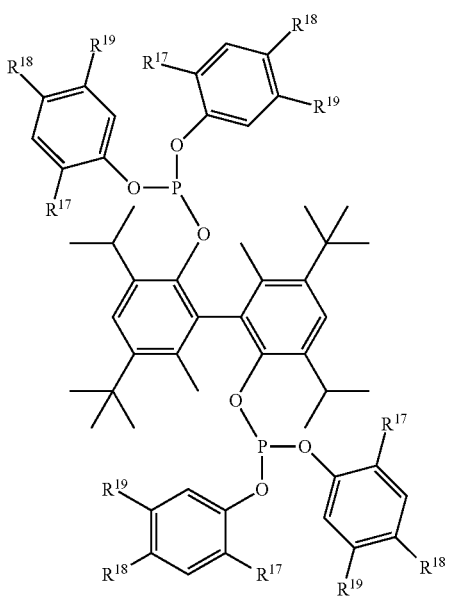
-continued

XXVI

18
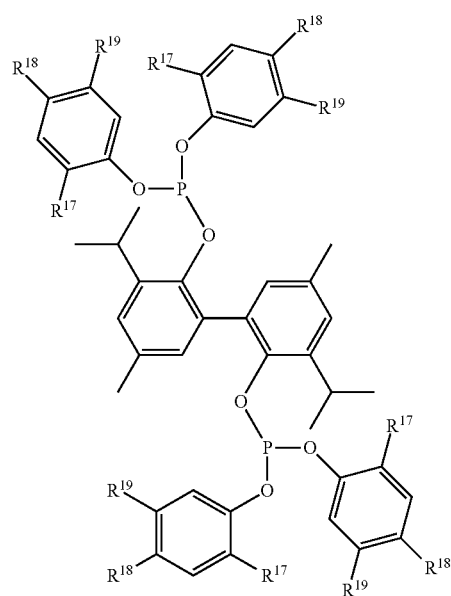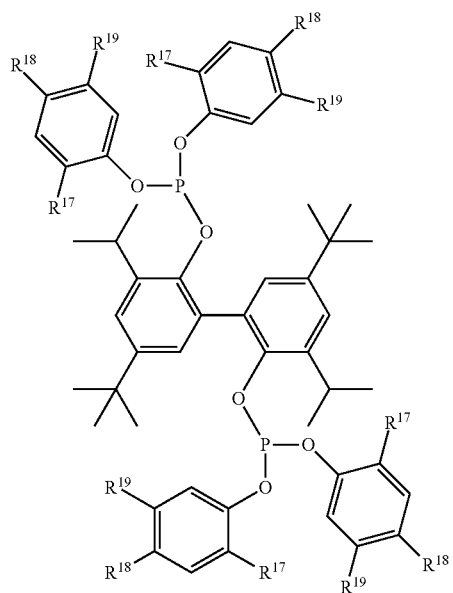
-continued

XXVIII
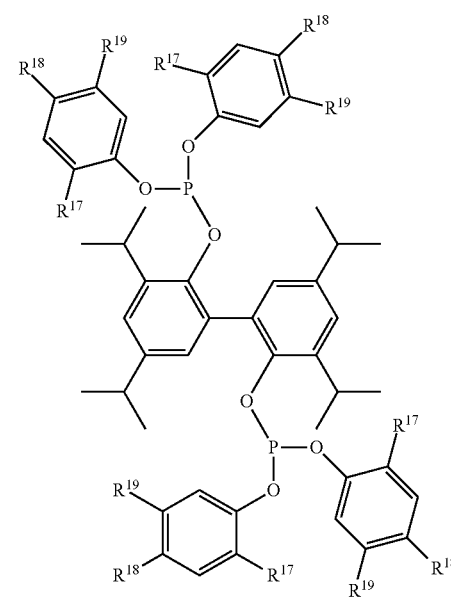
XXVII

XXIX

19
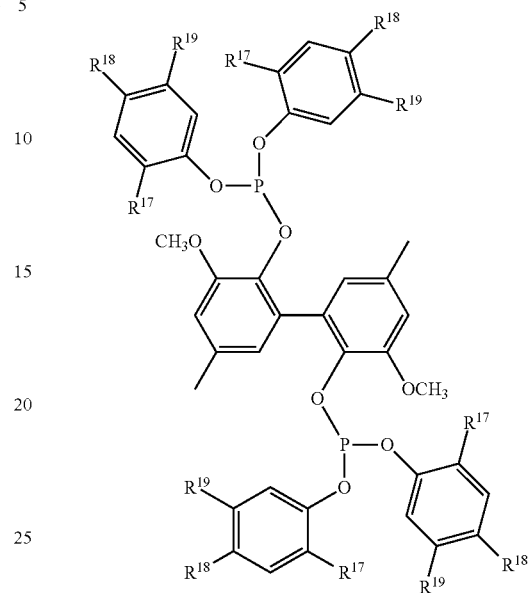
-continued

20

-continued

XXX

XXXII

XXXI
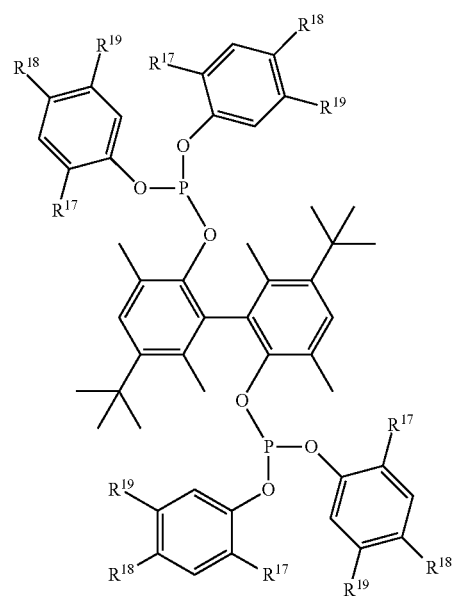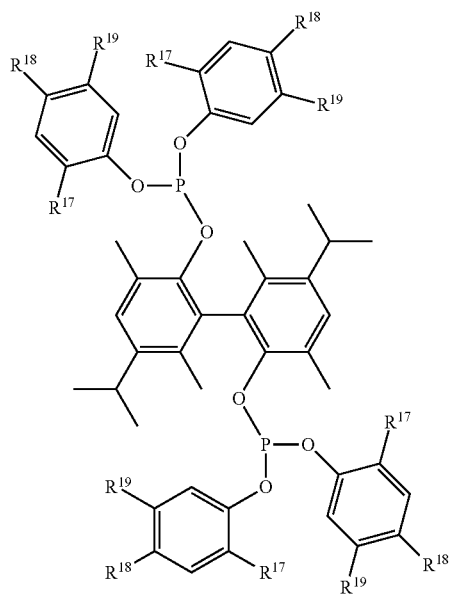

XXXIII
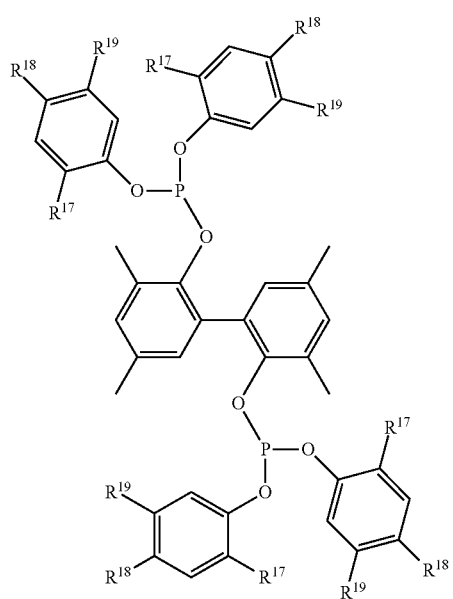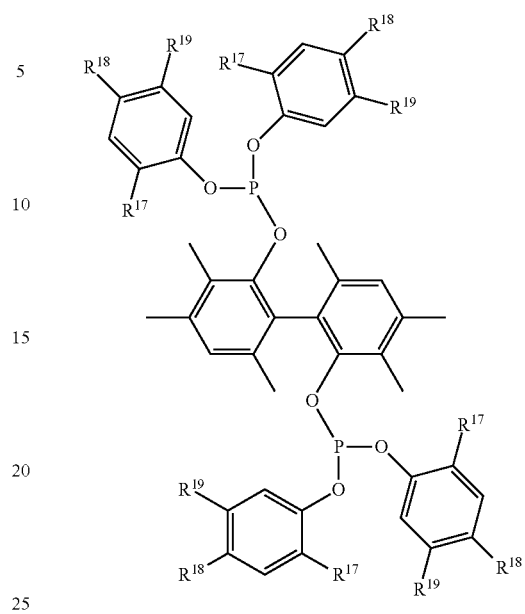
21
-continued

22
-continued
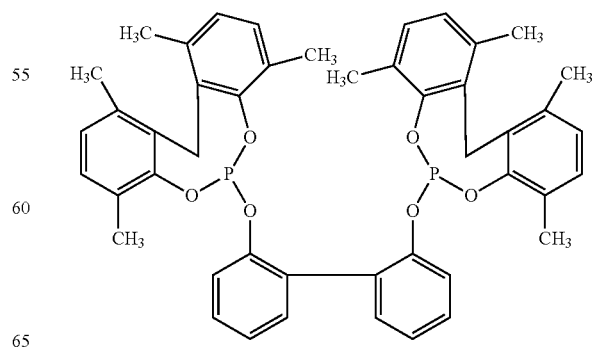
XXXIV

XXXVI

XXXVII

XXXV

XXXVIII
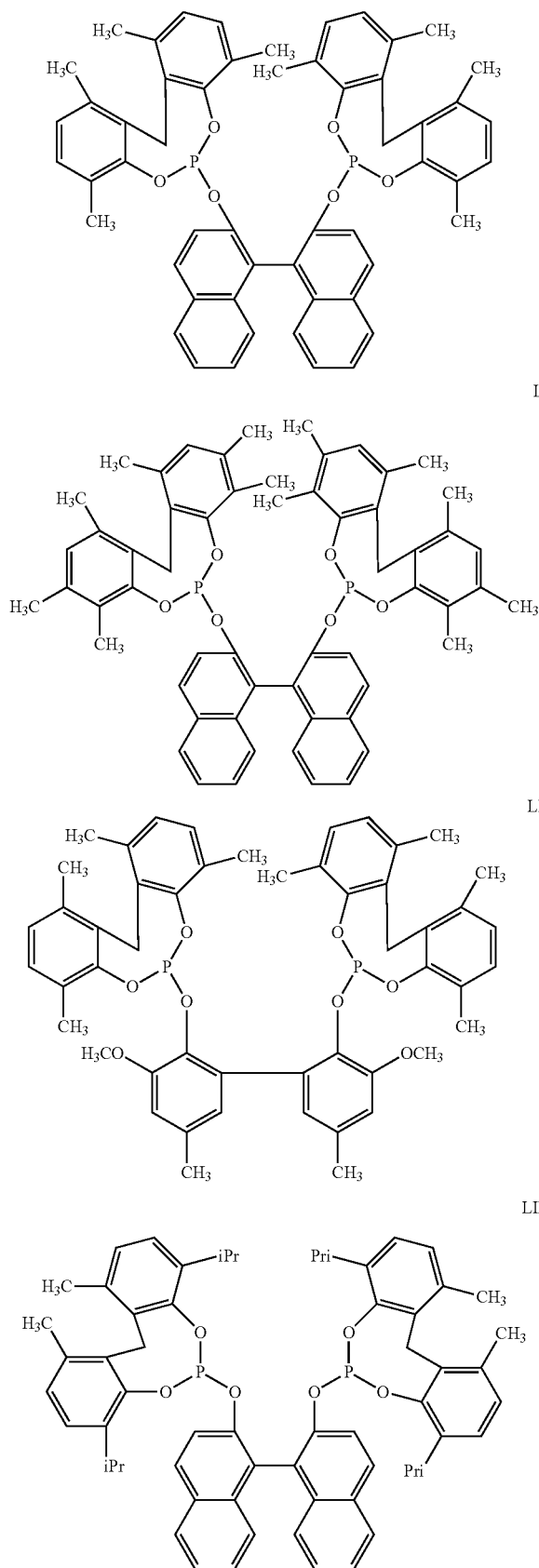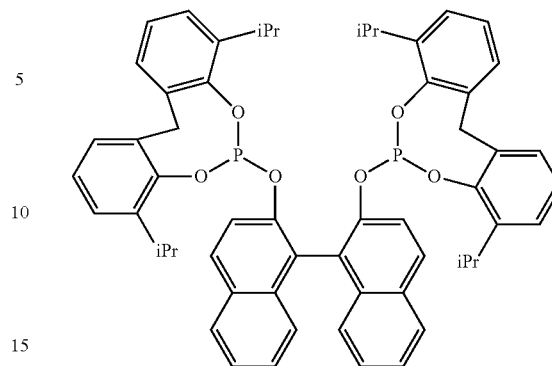
-continued

-continued

XXXIX

LIII

L

XXXIX

LI
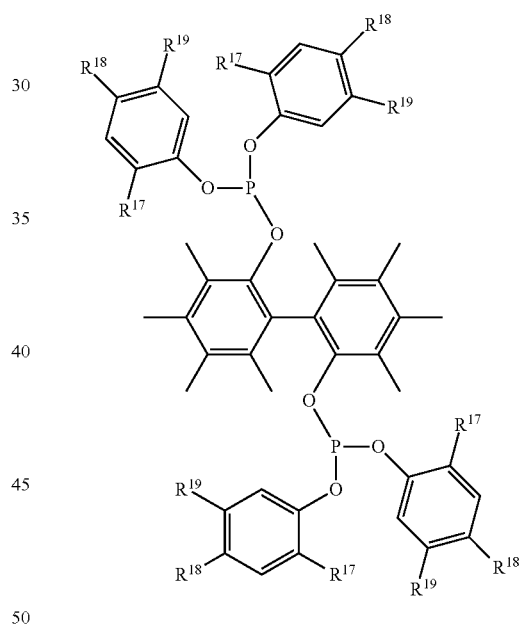
LII

Additional suitable bidentate phosphites are of the type disclosed in U.S. Pat. Nos. 5,512,695; 5,512,696; 5,663,369; 5,688,986; 5,723,641; 5,847,101; 5,959,135; 6,120,700; 6,171,996; 6,171,997; 6,399,534; the disclosures of which are incorporated herein by reference. Suitable bidentate phosphinites are of the type disclosed in U.S. Pat. Nos. 5,523,453 and 5,693,843, the disclosures of which are incorporated herein by reference.

Extraction Solvent

Suitable hydrocarbon extraction solvents include paraffins and cycloparaffins (aliphatic and alicyclic hydrocarbons) having a boiling point in the range of about 30° C. to about 135° C., including n-pentane, n-hexane, n-heptane and n-octane, as well as the corresponding branched chain paraffinic hydrocarbons having a boiling point within the range specified. Useful alicyclic hydrocarbons include cyclopentane, cyclohexane and cycloheptane, as well as alkyl substituted alicyclic hydrocarbons having a boiling point within the specified range. Mixtures of hydrocarbons may also be used, such as, for example, mixtures of the hydrocarbons noted above or commercial heptane which contains a number of hydrocarbons in addition to n-heptane. Cyclohexane is the preferred extraction solvent.

The lighter (hydrocarbon) phase recovered from the multistage countercurrent liquid-liquid extractor is directed to suitable equipment to recover catalyst, reactants, etc. for recycle to the hydrocyanation, while the heavier (lower) phase containing dinitriles recovered from the multistage countercurrent liquid-liquid extractor is directed to product recovery after removal of any solids, which may accumulate in the heavier phase. These solids may contain valuable components which may also be recovered, e.g., by the process set forth in U.S. Pat. No. 4,082,811.

EXAMPLES

In the following examples, values for extraction coefficient are the ratio of weight fraction of catalyst in the extract phase (hydrocarbon phase) versus the weight fraction of catalyst in the raffinate phase (organonitrile phase). An increase in extraction coefficient results in greater efficiency in recovering catalyst. As used herein, the terms, light phase, extract phase and hydrocarbon phase, are synonymous. Also, as used herein, the terms, heavy phase, organonitrile phase and raffinate phase, are synonymous.

Analysis of the extract and the raffinate streams of the catalyst extraction was conducted on an Agilent 1100 series HPLC and via ICP. The HPLC was used to determine the extraction efficiency of the process.

Example 1

To a 50 mL, jacketed, glass laboratory extractor, equipped with a magnetic stirbar, digital stir-plate, and maintained at 65° C., was charged 10 grams of the product of a pentenenitrile-hydrocyanation reaction, and 10 grams of the extract from the second stage of a mixer-settler cascade, operated in counter-current flow. This extract from the second stage comprised approximately 50 ppm nickel and 3100 ppm diphosphite ligand. The hexamethylene diamine concentration in the system was 0 ppm.

The reactor product was approximately:

85% by weight C_6 dinitriles

14% by weight C_5 mononitriles

1% by weight catalyst components

200 ppm by weight active nickel

230 ppm by weight zinc.

The laboratory reactor was then mixed at 500 rotations-per-minute, for 10 minutes, and then allowed to settle for 1 minute. After settling for 1 minute, a stable emulsion was present throughout the extract phase. Samples were obtained of the extract and raffinate phases of the extractor and analyzed to determine the extent of catalyst extraction. The ratio of active nickel present in the extract phase vs. the raffinate phase was found to be 5. The concentration of zinc in the raffinate was found to be 230 ppm.

Example 2

Example 1 was repeated except that hexamethylene diamine (HMD) was added to the system. In particular, a sufficient amount of HMD was added so that the molar ratio of Zn/HMD was 12 in the system.

Example 3

Example 1 was repeated except that hexamethylene diamine (HMD) was added to the system. In particular, a sufficient amount of HMD was added so that the molar ratio of Zn/HMD was 6 in the system.

Example 4

Example 1 was repeated except that hexamethylene diamine (HMD) was added to the system. In particular, a sufficient amount of HMD was added so that the molar ratio of Zn/HMD was 2.4 in the system.

Example 5

Example 1 was repeated except that hexamethylene diamine (HMD) was added to the system. In particular, a sufficient amount of HMD was added so that the molar ratio of Zn/HMD was 1.2 in the system.

Example 6

Example 1 was repeated except that bis-hexamethylene triamine (BHMT) was added to the system. In particular, a sufficient amount of BHMT was added so that the molar ratio of Zn/BMHT was 5.9 in the system.

Example 7

Example 1 was repeated except that bis-hexamethylene triamine (BHMT) was added to the system. In particular, a

sufficient amount of BHMT was added so that the molar ratio of Zn/BMHT was 2.9 in the system.

Example 8

Example 1 was repeated except that bis-hexamethylene triamine (BHMT) was added to the system. In particular, a sufficient amount of BHMT was added so that the molar ratio of Zn/BMHT was 1.2 in the system.

Example 9

Example 1 was repeated except that bis-hexamethylene triamine (BHMT) was added to the system. In particular, a sufficient amount of BHMT was added so that the molar ratio of Zn/BMHT was 12 in the system.

Example 10

Example 1 was repeated except that DCH was added to the system. In particular, a sufficient amount of DCH was added so that the molar ratio of Zn/DCH was 1.6 in the system.

Example 11

Example 1 was repeated except that DCH was added to the system. In particular, a sufficient amount of DCH was added so that the molar ratio of Zn/DCH was 2 in the system.

Example 12

Example 1 was repeated except that DCH was added to the system. In particular, a sufficient amount of DCH was added so that the molar ratio of Zn/DCH was 4 in the system.

Example 13

Example 1 was repeated except that DCH was added to the system. In particular, a sufficient amount of DCH was added so that the molar ratio of Zn/DCH was 8 in the system.

Example 14

Example 1 was repeated except that triethylamine (TEA) was added to the system. In particular, a sufficient amount of TEA was added so that the molar ratio of Zn/TEA was 1 in the system.

Example 15

Example 1 was repeated except that octylamine was added to the system. In particular, a sufficient amount of octylamine was added so that the molar ratio of Zn/octylamine was 1.3 in the system.

Comparative Example 16

Example 1 was repeated except that polyethyleneglycol (PEG-600) was added to the system. In particular, a sufficient amount of PEG-600 was added so that the molar ratio of Zn/PEG-600 was 1.5 in the system.

Comparative Example 17

Example 1 was repeated except that adipamide was added to the system. In particular, a sufficient amount of adipamide was added so that the molar ratio of Zn/adipamide was 2.3 in the system.

Comparative Example 18

Example 1 was repeated except that triphenyl phosphine (Ph$_3$P) was added to the system. In particular, a sufficient amount of Ph$_3$P was added so that the molar ratio of Zn/Ph$_3$P was 1 in the system.

Example 19

Example 1 was repeated except that calcium hydroxide (Ca(OH)$_2$) was added to the system. In particular, a sufficient amount of Ca(OH)$_2$ was added so that the molar ratio of Zn/Ca(OH)$_2$ was 0.3 in the system.

Results of Examples 1-19 are summarized in Table 1.

TABLE 1

Ex./CEx.	Temp (° C.)	Time (min)	Zn/Additive	Additive	KLL	Zn/Ni
1	65	10		None	5	1.15
2	65	10	12.0	HMD	13	1.09
3	65	10	6.0	HMD	13	1.11
4	65	10	2.4	HMD	23	0.43
5	65	10	1.2	HMD	84	0.12
6	65	10	5.9	BHMT	102	0.12
7	65	10	2.9	BHMT	80	0.17
8	65	10	1.2	BHMT	112	0.17
9	65	10	12.0	BHMT	18	
10	65	10	1.6	DCH	119	0.85
11	65	10	2	DCH	114	
12	65	10	4	DCH	27	1.03
13	65	10	8	DCH	8	1.05
14	65	10	1	TEA	20	0.94
15	65	10	1.3	Octylamine	63	0.96
16	65	10	1.5	PEG-600	5	1.07
17	65	10	2.3	Adipamide	6	
18	65	10	1	Ph$_3$P	4	1.15
19	65	10	0.3	Ca(OH)$_2$	14	

KLL = amount of catalyst in the extract/amount of catalyst in the raffinate;
Zn/Additive = the molar ratio of the zinc-to-additive during extraction;
Zn/Ni = the ratio of the total amount of zinc-to-nickel remaining in both phases after the extraction, as determined by inductively coupled plasma spectrometry (ICP).

The data summarized in Table 1 represent evaluations of a number of materials as potential additives for improved catalyst extraction. Examples 1-5 show the beneficial effect of hexamethylene diamine (HMD) on catalyst extraction, as the HMD loading increases (represented by decreasing Zn/Additive ratio) the catalyst extraction efficiency (represented by KLL) increases. Examples 6-9 show the beneficial effect of bis-hexamethylene triamine (BHMT) on catalyst extraction. Examples 10-13 show the beneficial effect of DCH on catalyst extraction. Example 15 shows the beneficial effect of adding octylamine on catalyst extraction. Example 19 shows the beneficial effect of calcium hydroxide on catalyst extraction. By way of contrast, Comparative Examples 16-18 show little effect on catalyst extraction using PEG-600, adipamide, and triphenyl phosphine, respectively.

Examples 20-25

These Examples 20-25 illustrate that effective catalyst recovery occurs for a mononitrile to dinitrile ratio greater than 0.65.

Five different mixtures comprised of a Ni diphosphite complex, with the diphosphite ligand shown in Structure XX (where R^{17} is isopropyl, R^{18} is H, and R^{19} is methyl), ZnCl$_2$ (equimolar with Ni) and differing in the ratio of mononitrile to dinitrile, were separately liquid-liquid batch extracted with an equal weight of cyane (i.e. cyclohexane). The molar ratio of organic mononitrile to organic dinitrile and the resulting

extraction coefficients are shown in the Table 2 below. A compound may be effectively recovered if it has an extraction coefficient of 1 or greater at solvent to feed ratios greater than 1 using a countercurrent multistage extractor.

TABLE 2

Catalyst and ligand extraction coefficients for varying ratios of mononitriles-to-dinitriles

Example	mononitrile/dinitrile	Catalyst extraction coefficient	Ligand extraction coefficient
1	2.33	1.28	4.09
2	1.85	1.33	8.08
3	1.19	2.02	16.97
4	0.91	2.63	35.99
5	0.57	4.82	49.59

Example 26

This Example demonstrates the effect of hold-up time on the extractability of the diphosphite ligand catalyst.

A mixture comprised predominantly of organic dinitriles and a Ni diphosphite complex, the structure of the diphosphite ligand being shown in Structure XX (where R^{17} is isopropyl, R^{18} is H, and R^{18} is methyl) and ZnCl$_2$ (equimolar with Ni) was divided into two portions. Both portions are liquid-liquid extracted in a three-stage contactor at 40° C., with an equal weight of cyclohexane. Both portions were sampled with time and the progress of the catalyst recovery into the extract phase is shown in Table 3 as the percent of the final steady state value achieved at a given time.

TABLE 3

Concentration of Diphosphite ligand with time in the extracting solvent phase.

Time, minutes	% of steady state concentration at 40° C.
2	12
4	19
8	34
14	52
30	78
60	100
91	100

Example 27

This Example illustrates the effect of temperature on the extractability of catalyst with first-stage extraction solvent recycle.

A mixture comprised predominantly of organic dinitriles and a Ni diphosphite complex, the structure of the diphosphite ligand being shown in Structure XXIV (where R^{17} is methyl, R^{18} is methyl and R^{19} is H) and ZnCl$_2$ (equimolar with Ni) was divided into three portions. The portions were batch liquid-liquid extracted at 50° C., 65° C. and 80° C., respectively, with an equal weight of n-octane and monitored with time. The results are shown in Table 4.

TABLE 4

Time	% of steady state at 50° C.	% of steady state at 65° C.	% of steady state at 80° C.
2	0.0	0.0	1.8
4	0.0	0.0	1.6
8	0.0	0.0	3.6
14	0.0	0.0	4.3
20	0.0	0.0	3.6
30	0.0	0.0	7.6
60	0.0	1.6	16.3
90	0.7	4.0	48.6

Example 28

This Example demonstrates the effect of adding water in three-stage extraction with cyclohexane recycle in the last stage.

Fifteen grams of a mixture comprised predominantly of organic dinitriles and a Ni diphosphite complex, the structure of the diphosphite ligand being shown in Structure XXIV (where R^{17} is methyl, R^{18} is methyl and R^{19} is H) and $ZnCl_2$ (equimolar with Ni), was extracted in a three-stage continuous extractor at a temperature of 50° C. with an equal weight of cyclohexane for one hour resulting in an catalyst extraction coefficient of 4.3, as measured by the amount of catalyst in the extract of the first stage divided by the amount of catalyst in the feed of the reaction mixture fed to the last stage of the three-stage countercurrent extractor.

To this mixture, 100 microliters of water was added. After continuing to heat and agitate for another hour, the diphosphite Ni extraction coefficient was measured as 13.4—a threefold increase.

Examples 29 and 30

These Examples demonstrate the effect of adding hexamethylene diamine (HMD) to the extraction zone.

Example 1 was repeated except that hexamethylene diamine was added to the product of a pentene-hydrocyanation reaction. To a 50 mL, jacketed, glass laboratory extractor, equipped with a magnetic stirbar, digital stir-plate, and maintained at 65° C., was charged 10 grams of the product of pentene-hydrocyanation reactor product, and 10 grams of the extract from the second stage of a mixer-settler cascade, operated in counter-current flow.

The reactor product was approximately:

85% by weight C_6 dinitriles

14% by weight C_5 mononitriles

1% by weight catalyst components

360 ppm by weight active nickel.

The laboratory reactor was then mixed at 1160 rotations-per-minute, for 20 minutes, and then allowed to settle for 15 minutes. A stable emulsion was present throughout the extract phase in the absence of the addition of HMD. After 15 minutes of settling, essentially no emulsion phase was present when HMD was added. Samples were obtained of the extract and raffinate phases of the extractor and analyzed to determine the extent of catalyst extraction.

TABLE 5

	Effect of hexamethylene diamine on catalyst extraction		
Example	Concentration of HMD added (ppm)	Catalyst recovery (KLL)	Stable emulsion
1	0	14	Yes
29	250	43	No
30	500	80	No

Examples 31-36

These Examples demonstrate the beneficial effect of adding hexamethylene diamine (HMD) on the reaction temperature required for catalyst extraction. For Examples 31-33, Example 1 was repeated, but the mixing time was 20 minutes, and the temperature was varied as indicated in Table 6. For Examples 34-36, Example 5 was repeated, and the temperature was varied as indicated in Table 6.

TABLE 6

Effect of hexamethylene diamine on temperature for catalyst extraction.			
Example	Temp (° C.)	KLL	Zn/HMD
31	65	16.76	No HMD
32	55	13.25	No HMD
33	45	8.06	No HMD
34	65	84.42	1.2
35	55	82.91	1.2
36	45	82.00	1.2

The data summarized in Table 6 represent evaluations of catalyst extraction performed at varying temperature from 45 to 65 degrees Celsius, with and without HMD present. Examples 31-33 show that catalyst extraction increases linearly with increasing temperature (represented by KLL). Examples 34-36 show that catalyst extraction does not require increased temperature when HMD added.

Examples 37-44

These Examples demonstrate the beneficial effect of adding hexamethylene diamine (HMD) on the mixing time required for catalyst extraction. For Examples 37-40, Example 31 was repeated, and the mixing time was varied as indicated in Table 7. For Examples 41-44, Example 5 was repeated, and the mixing time was varied as indicated in Table 7.

TABLE 7

Effect of hexamethylene diamine on mixing time required for catalyst extraction.			
Example	Mixing Time	KLL	Zn/HMD
37	20	16.13	No HMD
38	10	14.86	No HMD
39	5	14.49	No HMD
40	1	11.05	No HMD
41	10	84.42	1.2
42	5	114.34	1.2
43	1	98.24	1.2
44	0.5	56.23	1.2

The data summarized in Table 7 represent evaluations of catalyst extraction performed at varying mixing time from 20

minutes to 30 seconds, with and without HMD present. Examples 37-40 show that a decrease in catalyst extraction occurs when the mixing time is decreased to less than 5 minutes. Examples 41-44 show that catalyst extraction does not decrease until the mixing time is decreased to less than 1 minute, when HMD added.

What is claimed is:

1. A process for recovering diphosphite-containing compounds from a feed mixture comprising diphosphite-containing compounds, organic mononitriles, organic dinitriles and a Lewis acid in a multistage countercurrent liquid-liquid extractor with extraction solvent comprising aliphatic hydrocarbon, cycloaliphatic hydrocarbon or a mixture of aliphatic and cycloaliphatic hydrocarbon, said process comprising:

   a) flowing the feed mixture to the first stage of the multistage countercurrent liquid-liquid extractor; and

   b) contacting the feed mixture with extraction solvent in the multistage countercurrent liquid-liquid extractor, wherein the first stage of the multistage countercurrent liquid-liquid extractor comprises a mixing section and a settling section, wherein the mixing section provides a mixed phase comprising a light phase and a heavy phase, wherein a light phase separates from a heavy phase in the settling section, wherein a Lewis base is added to the mixing section of the first stage of the multistage countercurrent liquid-liquid extractor, wherein the light phase comprises extraction solvent and extracted diphosphite-containing compounds, wherein the heavy phase comprises organic mononitriles, organic dinitriles and a complex of said Lewis acid and said Lewis base, wherein at least a portion of the light phase is withdrawn from the settling section and treated to recover diphosphite-containing compounds extracted into the light phase, wherein at least a portion of the heavy phase is passed to the second stage of the multistage countercurrent liquid-liquid extractor, and wherein the Lewis base is selected from the group consisting of polyamines.

2. The process of claim 1, wherein the addition of Lewis base to the mixing section of the first stage of the multistage countercurrent liquid-liquid extractor is sufficient to result in enhanced settling of the light phase and heavy phase in the settling section of the first stage.

3. The process of claim 1, wherein the addition of Lewis base to the mixing section of the first stage of the multistage countercurrent liquid-liquid extractor is sufficient to achieve at least one of the following results: (a) a reduction in the size of an emulsion phase in the settling section, based upon the size of the emulsion phase in the absence of recycle of the heavy phase; (b) an increase in the rate of settling in the settling section, based upon the rate of settling in the absence of recycle of the heavy phase; (c) an increase in the amount of diphosphite-containing compounds in the light phase, based upon the upon the amount of diphosphite-containing compounds in the light phase in the absence of recycle of the heavy phase; (d) a reduction in the size of a rag layer in the settling section, based upon the size of a rag layer in the settling section in the absence of recycle of the heavy phase; and (e) reduction in the rate of formation of a rag layer in the settling section, based upon the rate of formation of a rag layer in the settling section in the absence of recycle of the heavy phase.

4. The process of claim 1, wherein the addition of Lewis base to the mixing settling section of the first stage is sufficient to result in improved extraction of diphosphite-contain-

ing compounds based upon the extraction of diphosphite compounds in the absence of recycle of addition of Lewis base.

5. The process of claim 1, wherein the addition of Lewis base to the mixing settling section of the first stage is sufficient to result in improved extraction of diphosphite-containing compounds based upon the extraction of diphosphite compounds in the absence of recycle of addition of Lewis base, at reduced temperature.

6. The process of claim 1, wherein the addition of Lewis base to the mixing settling section of the first stage is sufficient to result in improved extraction of diphosphite-containing compounds based upon the extraction of diphosphite compounds in the absence of recycle of addition of Lewis base, with reduced mixing time.
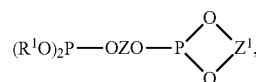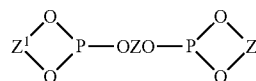
7. The process of claim 1, wherein the Lewis base is cofed to the mixing section along with the feed mixture comprising diphosphite-containing compounds, organic mononitriles, organic dinitriles and Lewis acid.

8. The process of claim 1, wherein the Lewis base is separately fed to the mixing section apart from the feed mixture comprising diphosphite-containing compounds, organic mononitriles, organic dinitriles and Lewis acid.

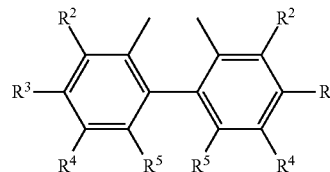9. The process of claim 1, wherein the Lewis acid is $ZnCl_2$.

10. The process of claim 1, wherein the extraction solvent feed from the second stage comprises at least 1000 ppm of diphosphite-containing compounds.

11. A process according to claim 1 wherein the diphosphite-containing compound is a Ni complex with a diphosphite ligand selected from the group consisting of:
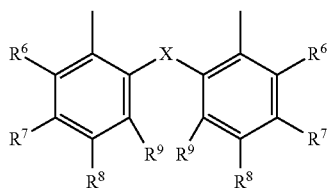
$$(R^1O)_2P(OZO)P(OR^1)_2, \qquad \text{I}$$

II

III

and

   wherein in I, II and Ill, R^1 is phenyl, unsubstituted or substituted with one or more C_1 to C_{12} alkyl or C_1 to C_{12} alkoxy groups; or naphthyl, unsubstituted or substituted with one or more C_1 to C_{12} alkyl or C_1 to C_{12} alkoxy groups; and wherein Z and Z^1 are independently selected from the group consisting of structural formulae IV, V, VI, VII, and VIII:
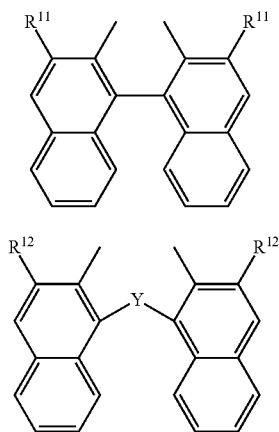

IV

-continued

V

and wherein

R^2, R^3, R^4, R^5, R^6, R^7, R^8, and R^9 are independently selected from the group consisting of H, C_1 to C_{12} alkyl, and C_1 to C_{12} alkoxy;

X is O, S, or $CH(R^{10})$;

R^{10} is H or C_1 to C_{12} alkyl;

VI

VII

and wherein

R^{11} and R^{12} are independently selected from the group consisting of H, C_1 to C_{12} alkyl, and C_1 to C_{12} alkoxy and CO_2R^{13},
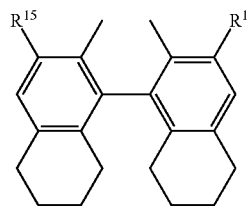
R^{13} is C_1 to C_{12} alkyl, or C_6 to C_{10} aryl unsubstituted or substituted with C_1 to C_4 alkyl;

Y is O, S, or $CH(R^{14})$;

R^{14} is H or C_1 to C_{12} alkyl;

VIII

wherein

R^{15} is selected from the group consisting of H, C_1 to C_{12} alkyl, and C_1 to C_{12} alkoxy and CO_2R^{16},

R^{16} is C_1 to C_{12} alkyl, or C_6 to C_{10} aryl, unsubstituted or substituted with C_1 to C_4 alkyl,

and wherein

for structural formulae I through VIII, the C_1 to C_{12} alkyl, and C_1 to C_{12} alkoxy groups may be straight chain or branched.

12. The process of claim **9**, wherein at least a portion of the diphosphite-containing compound is complexed with zero valent Ni.

13. The process of one of claim **1** wherein at least one stage of the extraction is carried out above 40° C.

14. The process of claim **13** wherein the polyamine comprises at least one selected from hexamethylene diamine and dimers and trimers of hexamethylene diamine.

15. The process of claim **13** wherein the polyamine comprises bis-hexamethylenetriamine.

16. The process of claim **1** wherein the extraction solvent is cyclohexane.

17. The process of claim **1** wherein the feed mixture is an effluent stream from a hydrocyanation process.

18. The process of claim **17** wherein the hydrocyanation process includes a 3-pentenenitrile hydrocyanation process.

19. The process of claim **17** wherein the hydrocyanation process includes a 1,3-butadiene hydrocyanation process.

20. The process of claim **1**, wherein the first stage of the multistage countercurrent liquid-liquid extractor takes place in an extraction column, wherein the entire column is a settling section comprising a mixing section between a heavy phase collection section and a light phase collection section, and wherein the Lewis base is added to the mixing section.

21. The process of claim **1**, wherein the first stage of the multistage countercurrent liquid-liquid extractor takes place in an mixer-settler, wherein the mixer-settler comprises a settling section which is separate from the mixing section, and wherein the Lewis base is added to the mixing section.

*   *   *   *   *